Metrology for Emerging Materials, Devices, and Structures: Graphene as an Example

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INDEX
INSTITUTE FOR NANOELECTRONICS
DISCOVERY AND EXPLORATION

Outline

- Characterization and Metrology
- Physical Properties of Graphene
- Optical Microscopy
- LEEM
- LEED
- HR-TEM
- Electrical Characterization
- Overriding Themes

Characterization and Metrology: Themes

- Nano-Scale and Quantum Phenomena

- Familiar Methods show a “new light”

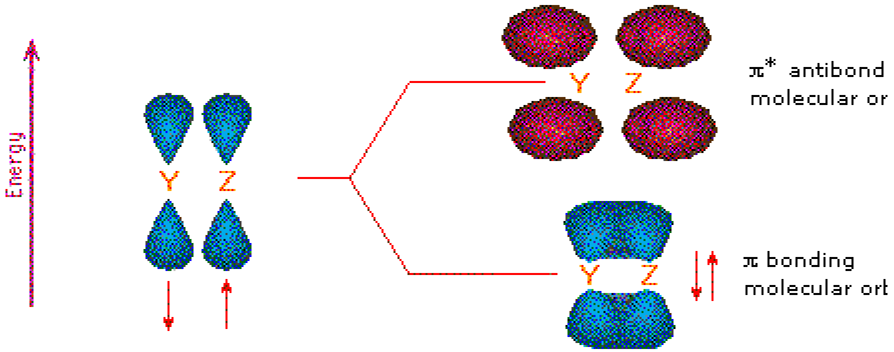
- New Methods always help

- Advancements still Required

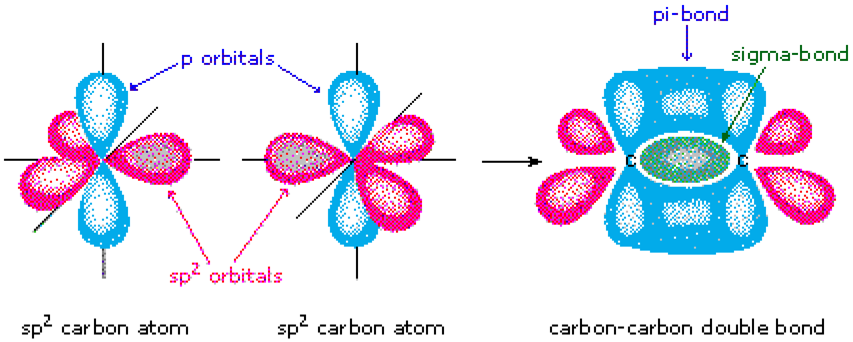
Properties of Graphene

- High Mobility
  ~ 100,000 cm^2/V sec (few degrees Kevin)
  ~ 10,000 cm^2/V sec (room temperature)
- Can carry high current density
- Robust Material

Graphene Band Structure

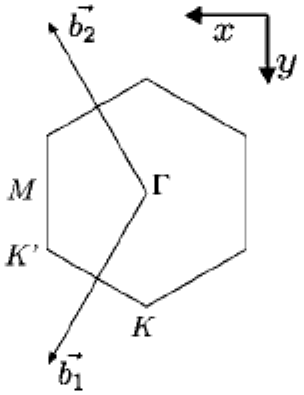


A π-orbital formation from two p-orbitals

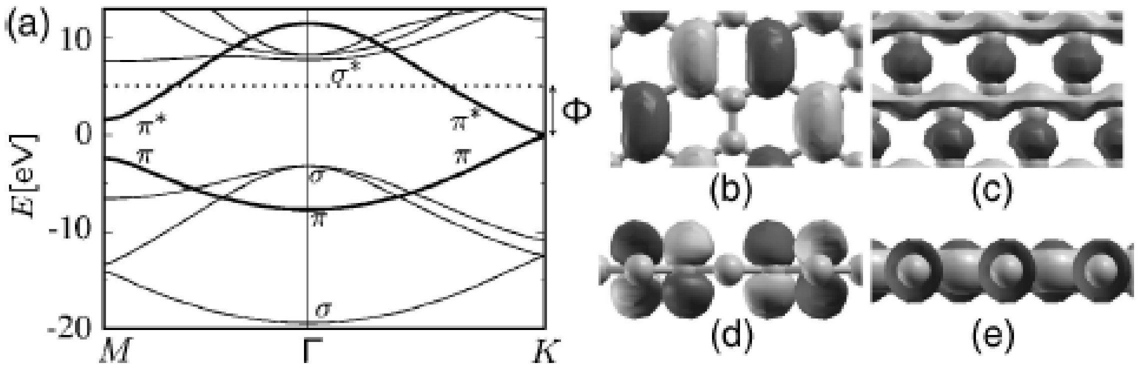


B Formation of σ- and π- molecular orbitals
from two sp^2 hybridized carbon atoms

www.cem.msu.edu/~reusch/VirtualText/intro3.htm



π state at K



π bond and π* anti-orbitals

Charlier et al REVIEWS OF MODERN PHYSICS, VOLUME 79, APRIL–JUNE 2007

Graphene Electrical Properties

- **Semiconductors**
  - **Parabolic Dispersion of Energy vs momentum**
  - **Effective Mass defined by change of E vs k**

$$E = \hbar^2 k^2/2m$$

$$m^* = \hbar^2 /(d^2 E/d^2 k)$$

- **Graphene**
  - **Linear Dispersion of energy levels vs momentum (wave vector k)**
  - **light-like linear electronic band dispersion implies massless particles**
  - **Particles called Dirac Fermions**

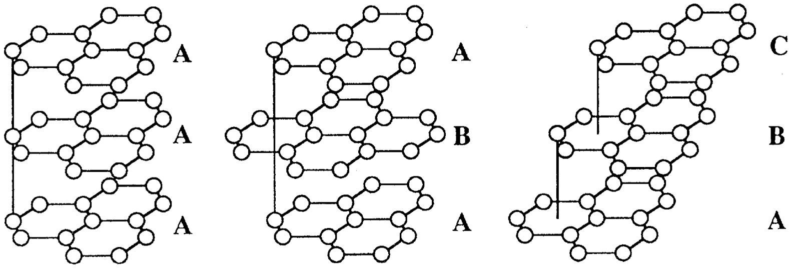
$$E^{\pm}(\delta\mathbf{k}) \simeq \pm(\sqrt{3}a/2)\gamma_0 \|\delta\mathbf{k}\|$$

$$v_F = \sqrt{3}a\gamma_0/2\hbar = \tfrac{3}{2}a_{cc}\gamma_0/\hbar$$

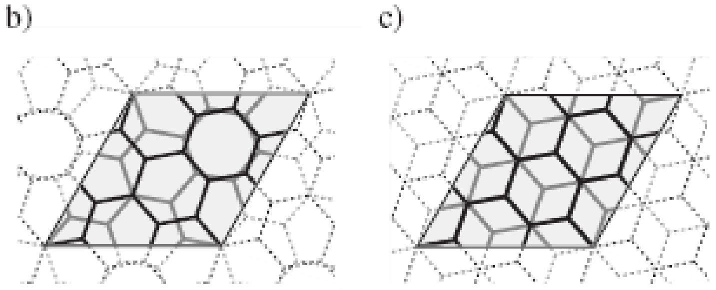
$$E = h\,c$$

See p 684 Charlier et al

Graphene



Bernal



turbostratic AA' supercell

Bernal AB supercell

38.21°

Sources of Graphene

Exfoliation – Scotch tape & graphite

Reaction of SiC(0001)

Other

Bernal Stacking vs Misorientation

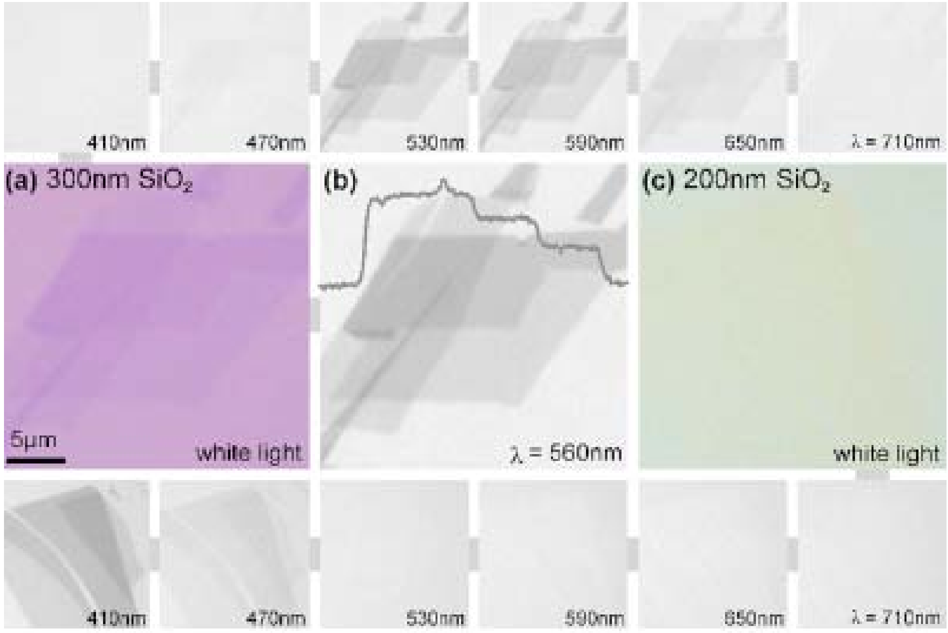
Single Layer Properties for misoriented (AA')
No-Dirac Fermions for 2 to 4 layer Bernal

Inter-layer spacin 3.33 Å for *B* and
3.42 Å for turbostratic stacked bi-layer

Other mis-orientations possible

Latil, Meunier, and Henrard, PRB 76, 201402_R (2007)

Optical Microscopy
The magic 300 nm SiO_2 substrate



Graphine is modeled
as a 0.34 nm thick graphite layer

Graphite refractive index constant
Between 400 nm to 750 nm

n = 2.6 – i 1.3

Contrast dependence is a result of wavelength dependence of SiO_2 reflectivity

SiO_2 reflectivity function
of SiO_2 thickness

Blake, et al., Appl. Phys. Lett. 91, (2007), 063124

Nano Scale Optical Properties

Optical Properties of Graphene defined solely by the Fine Structure Constant

- Dynamic Conductivity, $G = e^2/4h$, of Dirac Fermions
- Fine Structure Constant $\alpha = e^2/hc \approx 1/137$
- $T \equiv (1 + 2\pi G/c)^{-2} = (1 + \frac{1}{2}\pi\alpha)^{-2}$
- $R \equiv \frac{1}{4}\pi^2\alpha^2 T$

Nair et al, Manchester group in Science 320, (2008), 1308

Remember Surface Analysis Methods - LEEM

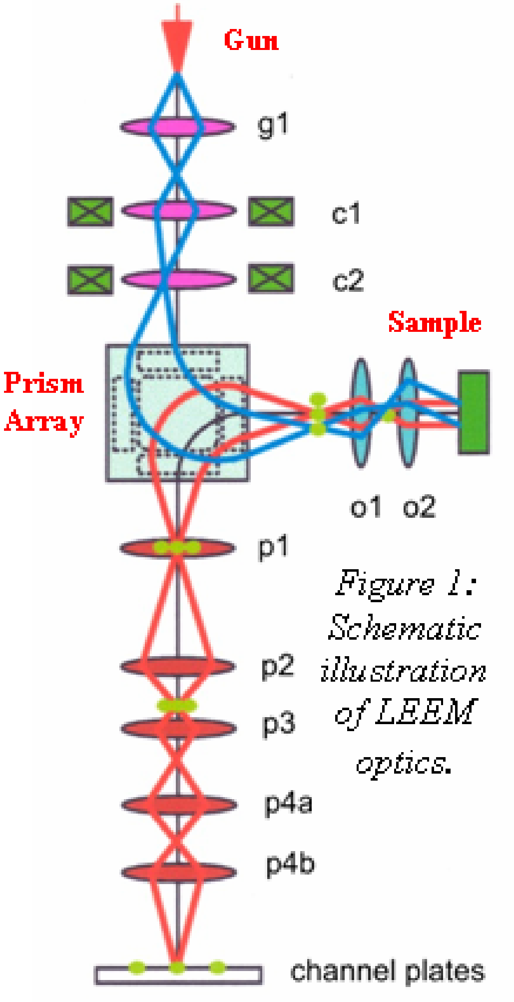
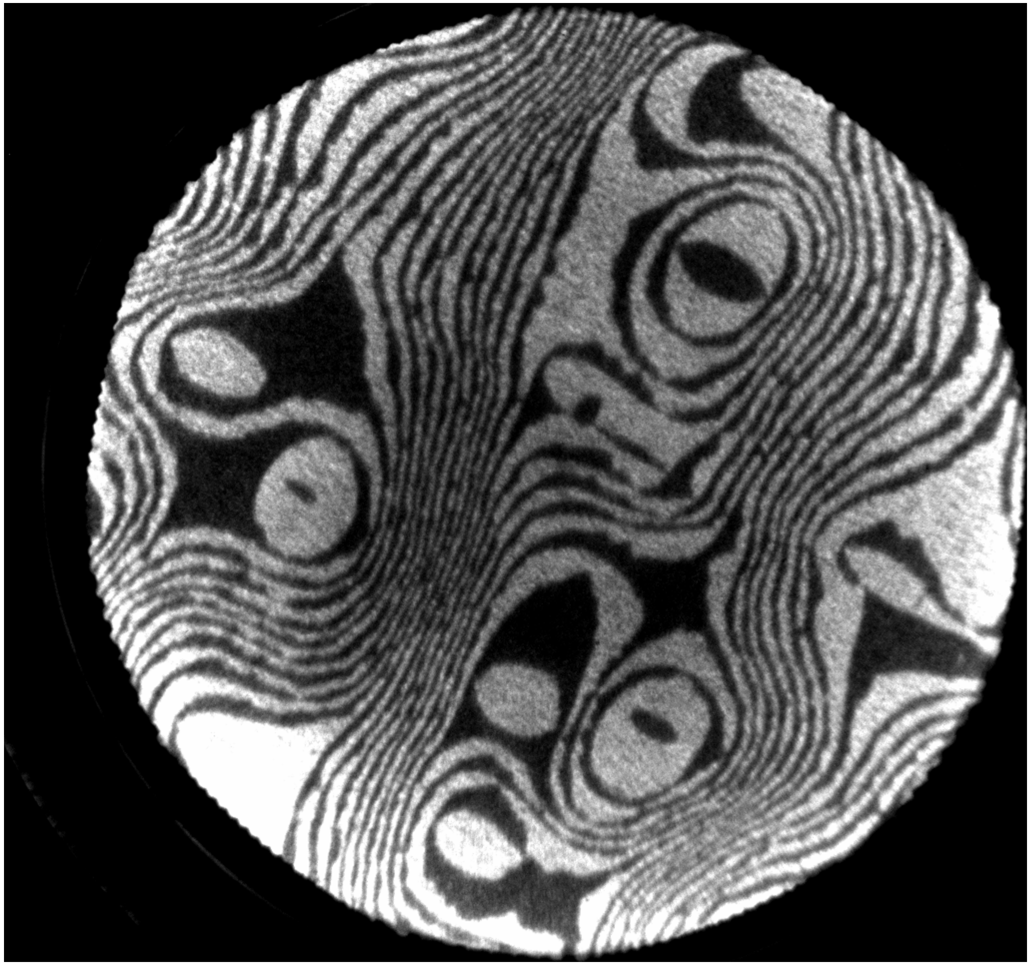


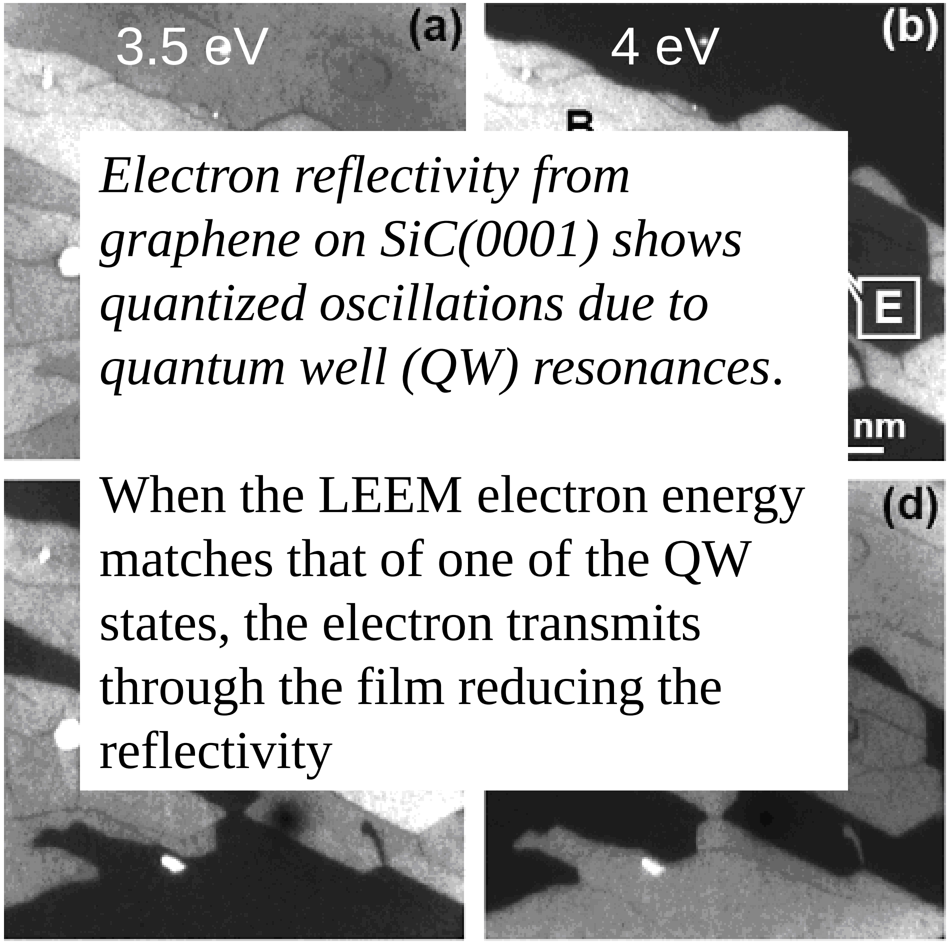
Figure 1: Schematic illustration of LEEM optics.



Monolayer Sensitivity

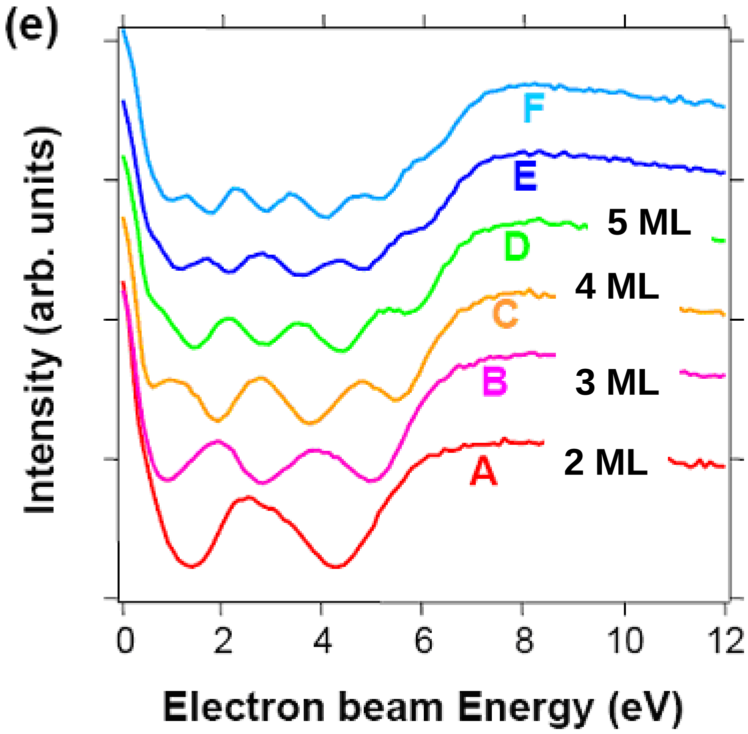
Figures from J. Thorp /UVa, R. Hull (INDEX)/RPI, R. Tromp /IBM

LEEM analysis of Multilayer Graphene



Electron reflectivity from graphene on SiC(0001) shows quantized oscillations due to quantum well (QW) resonances.

When the LEEM electron energy matches that of one of the QW states, the electron transmits through the film reducing the reflectivity

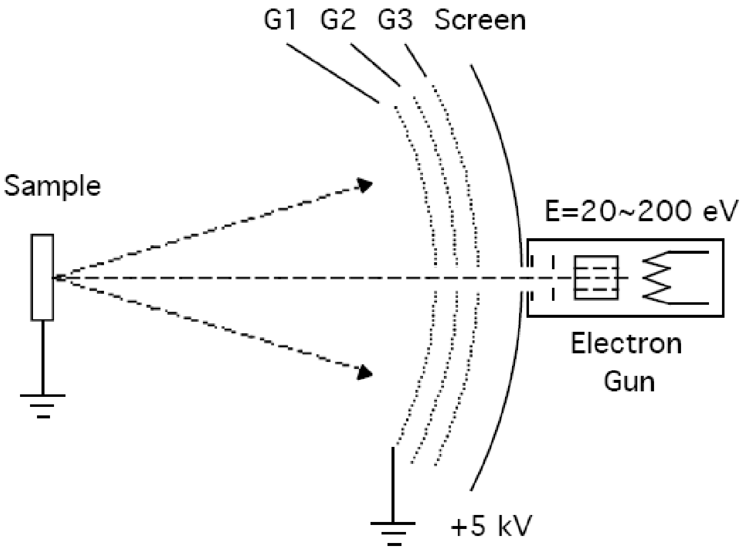


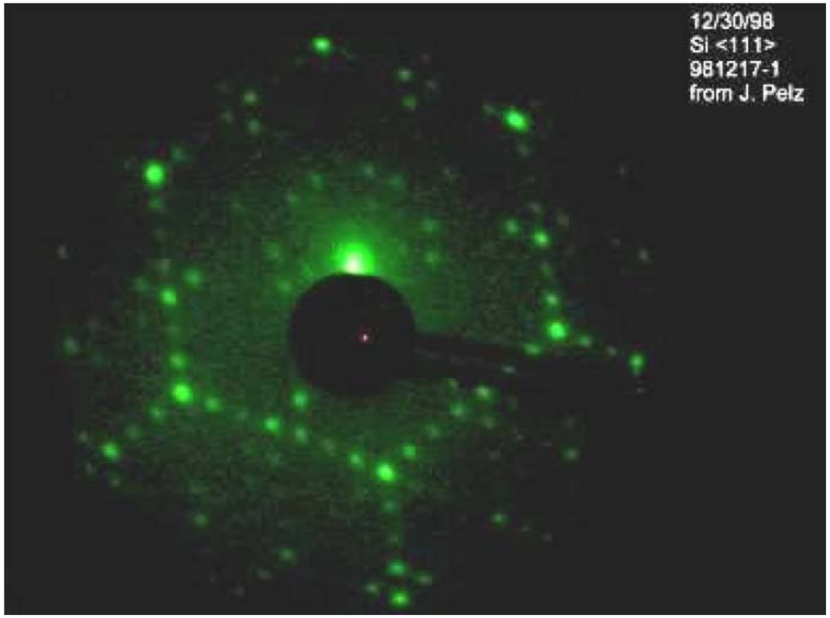
1 ML has one minimum in reflectance curve

Figure courtesy H. Hibino: Phys. Rev. B. 77, (2008), 075413.

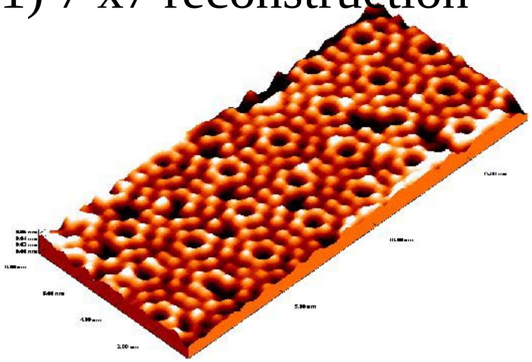
Remember Surface Analysis Methods - LEED

Low Energy Electron Diffraction



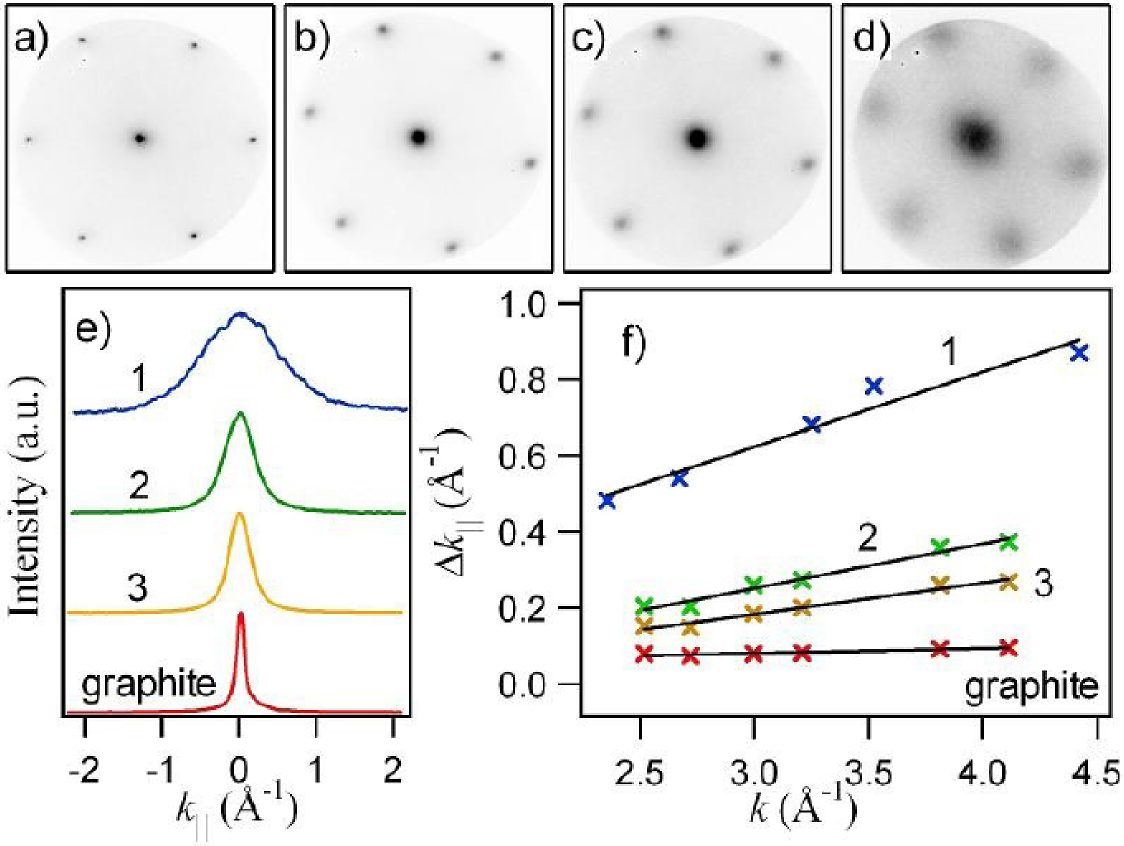


Si (111) 7 x7 reconstruction



NIST Surface Science Database & www.cem.msu.edu/~cem924sg/

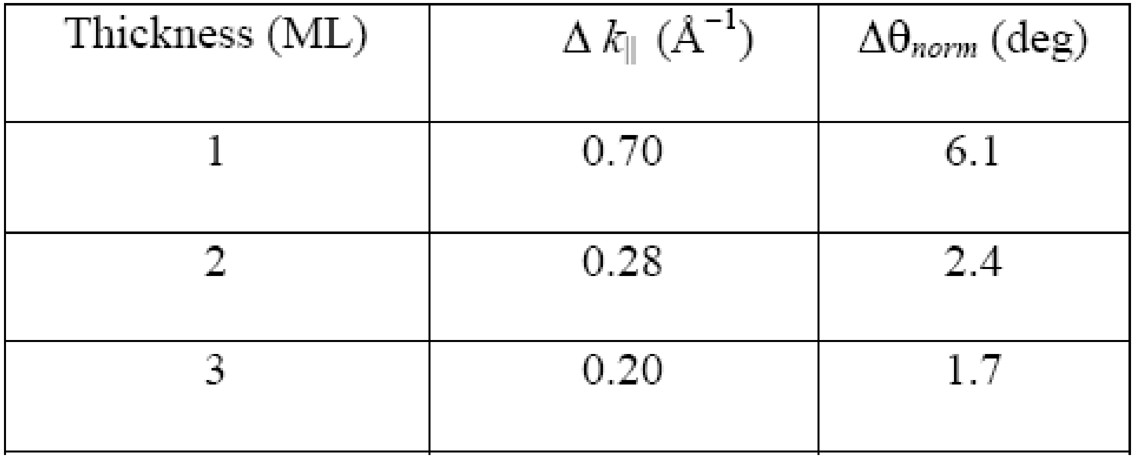
LEED Analysis of Graphene



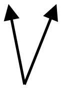
. 2 (a-d) Graphite, trilayer, bilayer, and monolayer graphene LEED patterns at 42 eV, respectively.

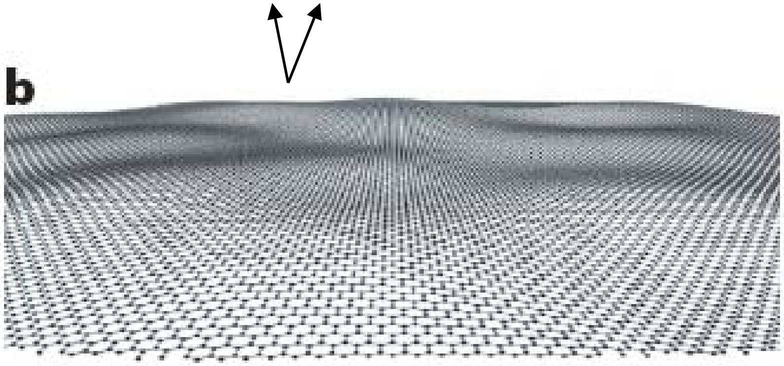
Knox (Osgood Group at Columbia) AVS 2009

LEED Analysis of Corrugation of Graphene



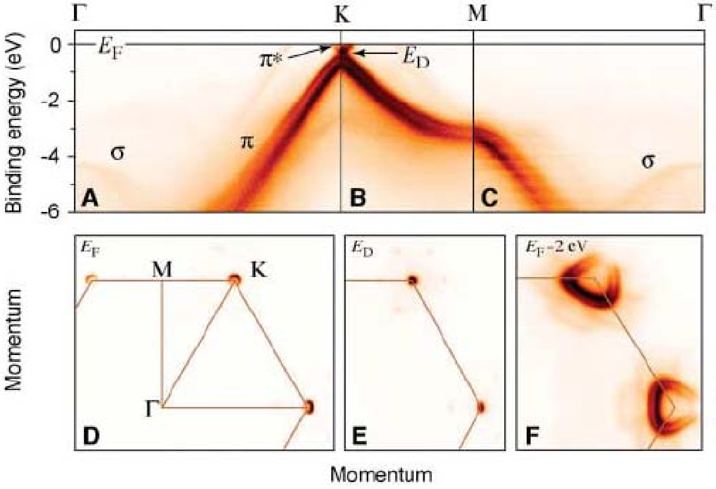
Thickness (ML)	$\Delta k_{\parallel}$ (Å^{-1})	$\Delta\theta_{norm}$ (deg)
1	0.70	6.1
2	0.28	2.4
3	0.20	1.7





Knox (Osgood Group at Columbia) AVS 2009

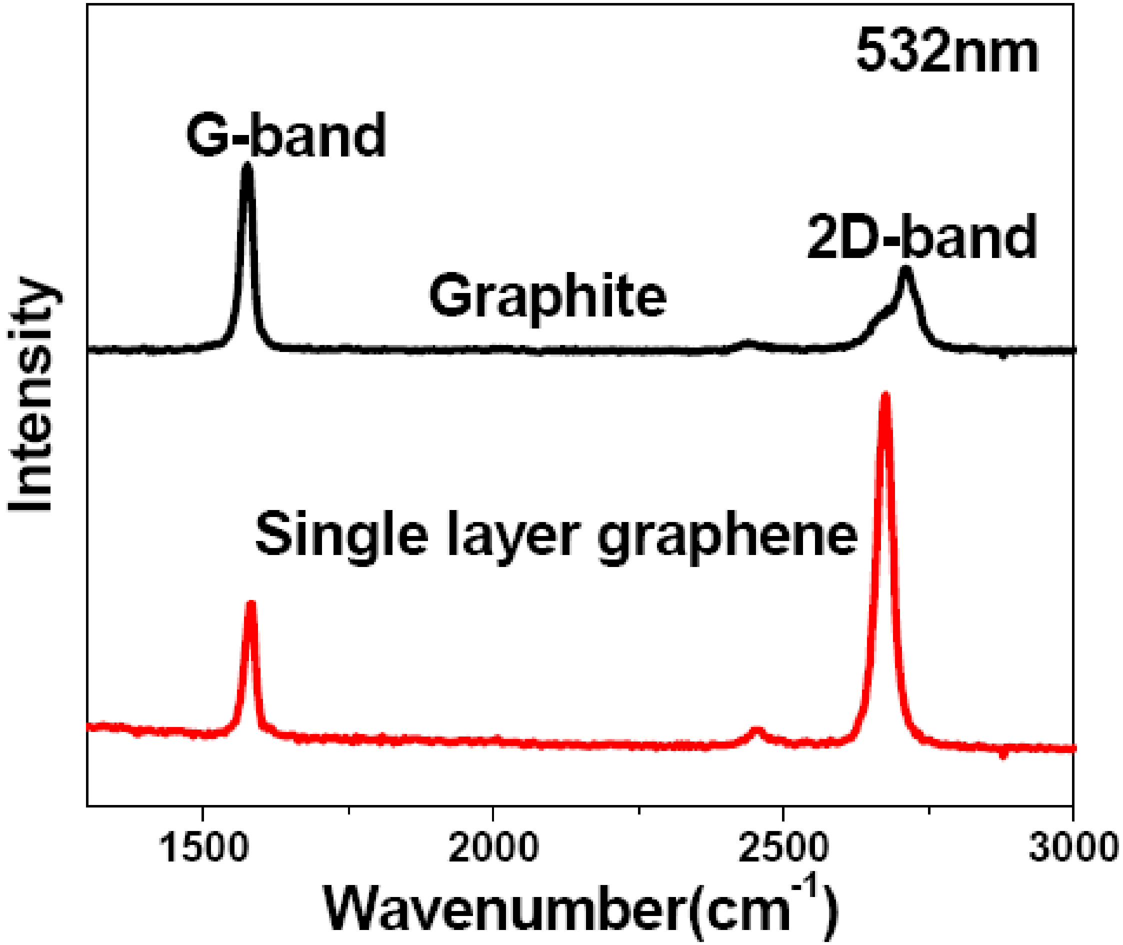
Remember Surface Analysis Methods – (AR)XPS



- ARXPS maps VB structure
- Bands not described by simple tight binding model
- Quasiparticles observed – e.g., electrons surrounded by phonons
- Potassium Doping opens band gap
- May explain impact of substrate on graphene electrical properties

Ohta, Bostwick, Seyller, Horn, & Rotenburg, Science 313, (2006), p 951 & Nature Physics 3 (2007), p 36.

Raman of Graphene

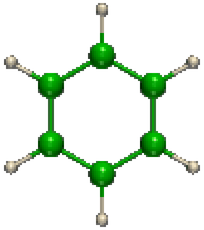


See for example: Ni Raman spectroscopy and imaging of graphene

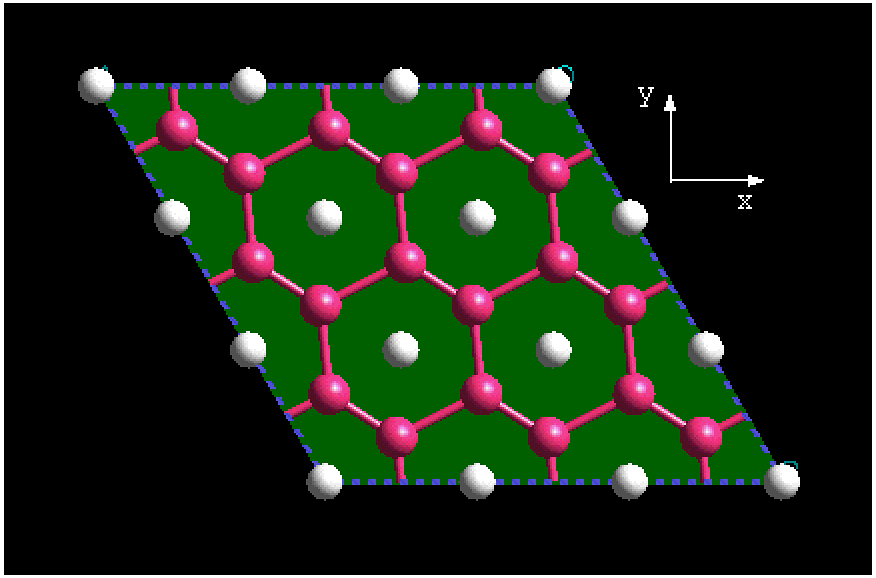
Raman of Graphene

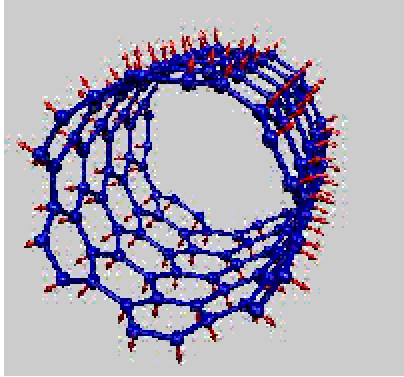
The molecular picture

D band attributed to the breathing modes of sp2-bonded atoms in rings



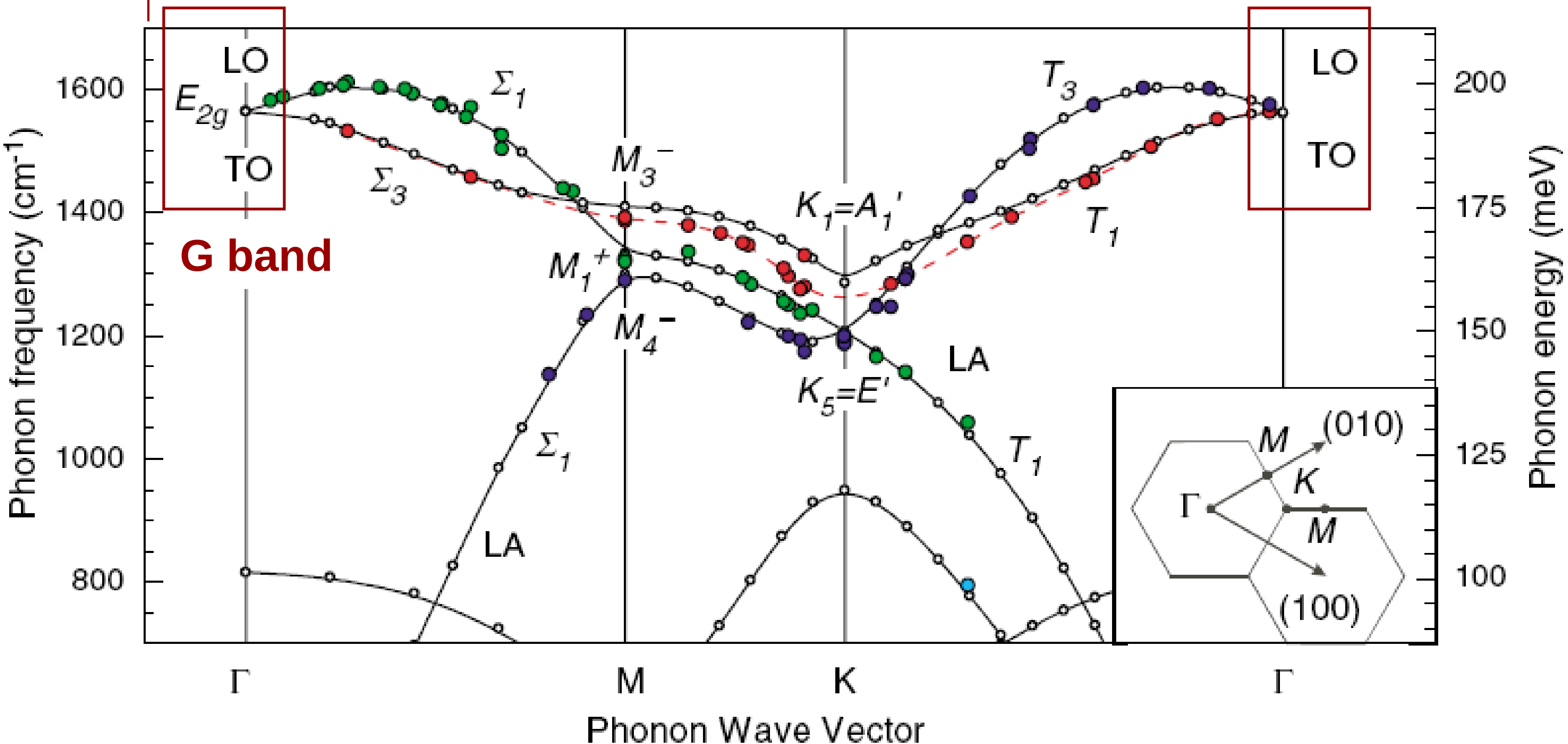
Benzene
Breathing Mode





Graphene’s Phonon Dispersion

2D band is at ~2700 cm^{-1} due to a 2 phonon double resonant process involving π band



G band

Wave vector K =0 Zone Center

J. Maultzsch et al, Phys. Rev. Lett. 92, (2004) 075501

Raman 2D Band Sensitive to # graphene layers

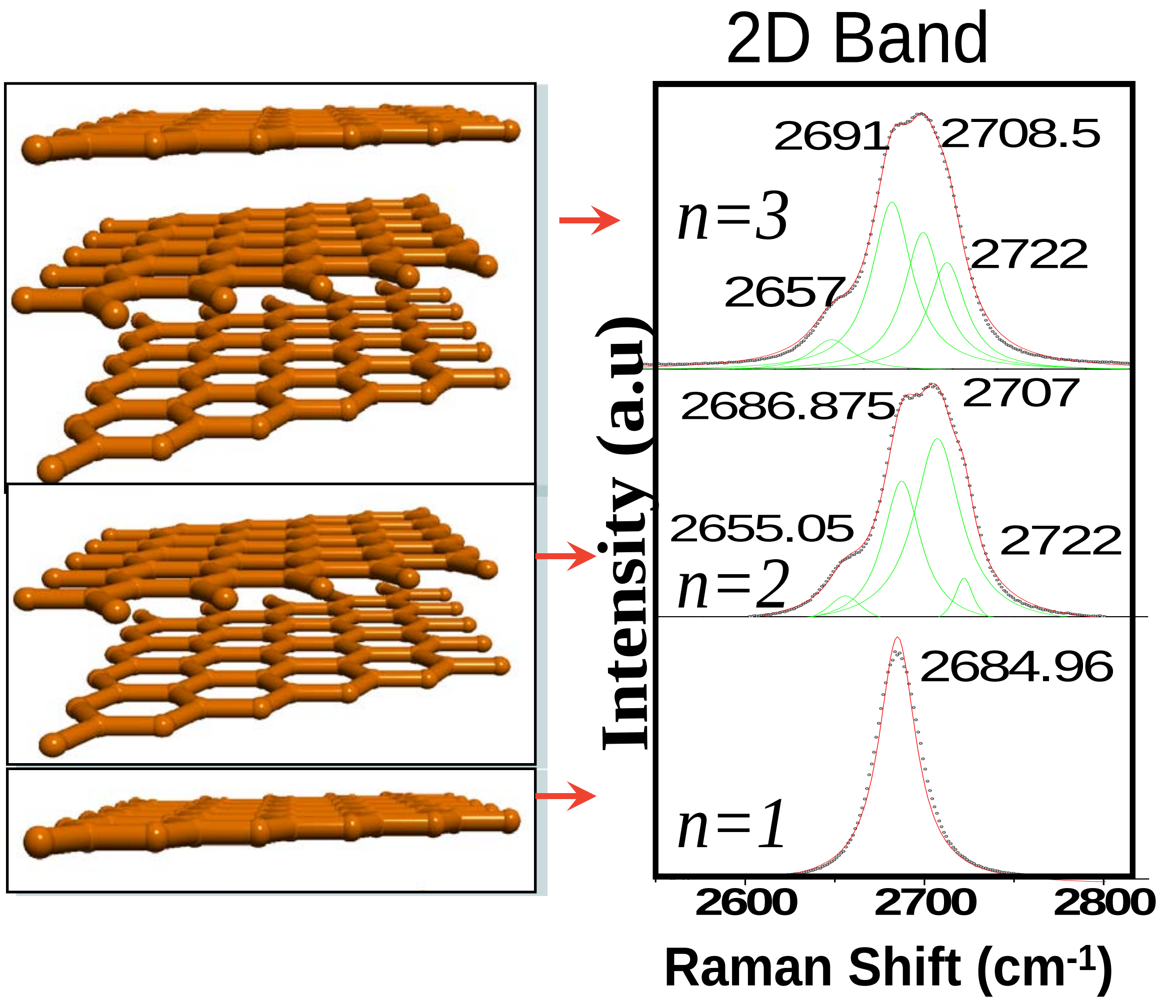
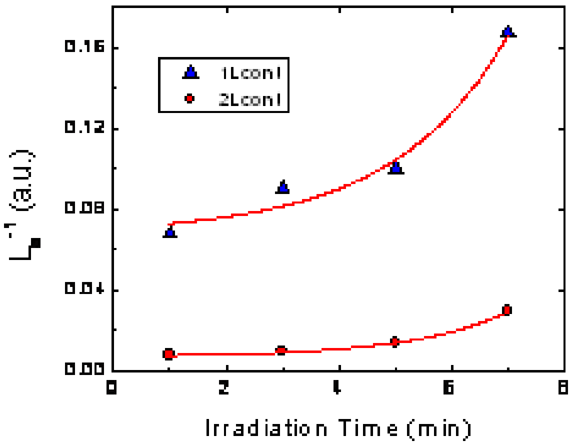


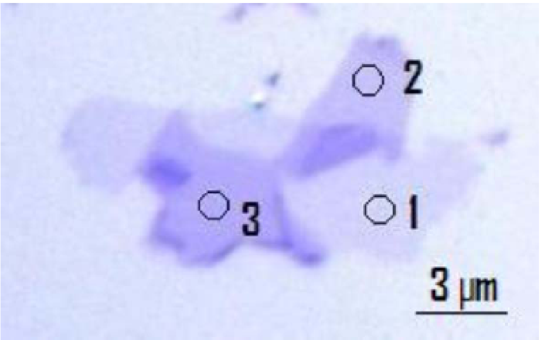
Figure Courtesy Robert Geer CNSE (INDEX)

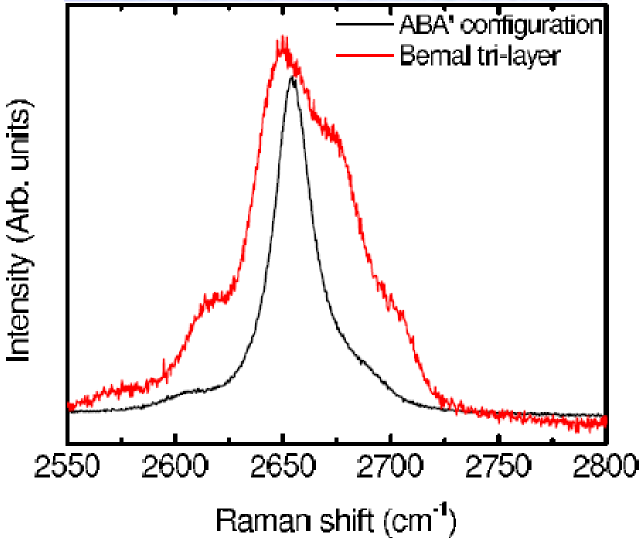
Raman:: Defects & Stacking Configuration



Electron irradiation induced defect density

L^{-1} proportional to Ratio of the intensities of G band to D band





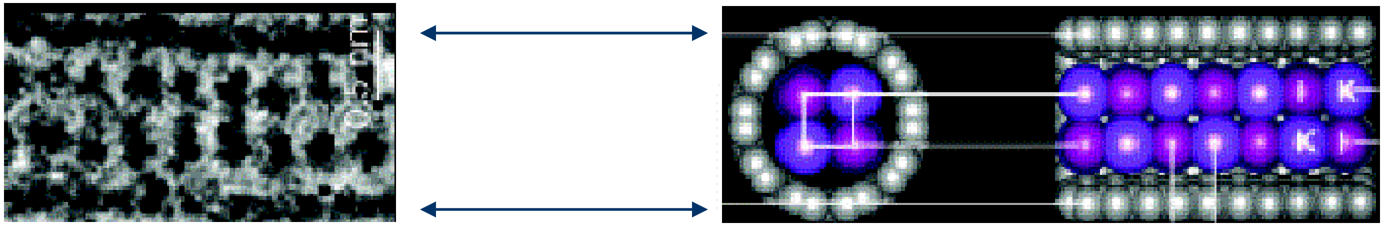
Geer Group unpublished

Poncharal, Phys. Rev. B 78, 113407 2008

NanoCharacterization of Nanotubes

Aberration Corrected HR-TEM Imaging

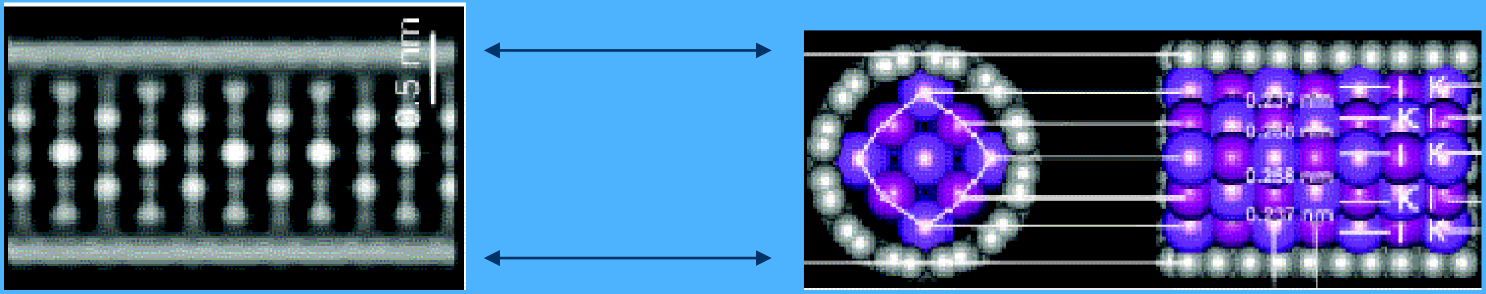
Not Corrected



Heavy atom (Iodine) atomic columns are imaged

Focal Series Corrected

Atomic Columns

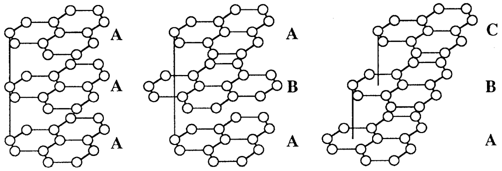


I K
K I
I K
K I
I K

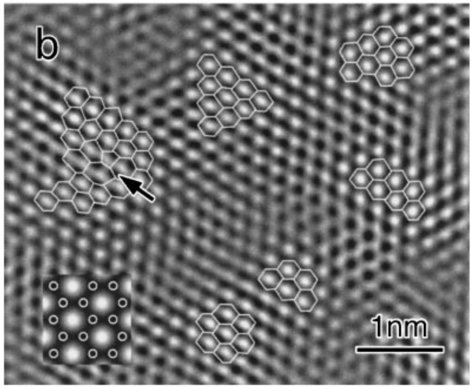
Both K and I atomic columns are imaged

Sloan, et al, MRS Bulletin, April 2004

Multi-Slice Simulations of Graphene Stacking

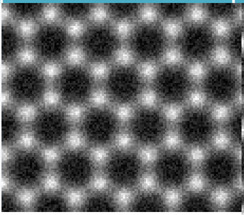
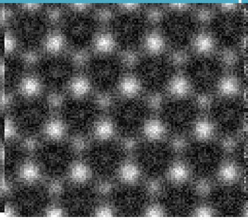
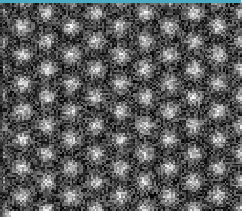


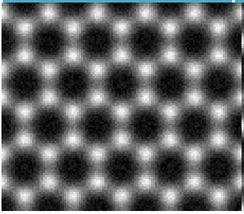
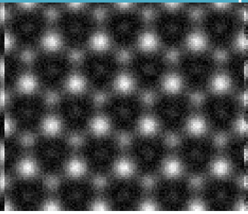
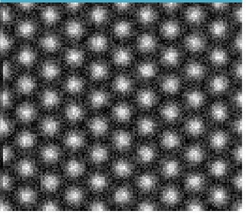
Carbon Nanofilm



Horiuchi, et al.

*C5=5mm, 0.15 Convergence angle

	AAA	ABA	ABC
-150A Defocus, 4% Noise			

	AAA	ABA	ABC
-150A Defocus, 2% Noise			

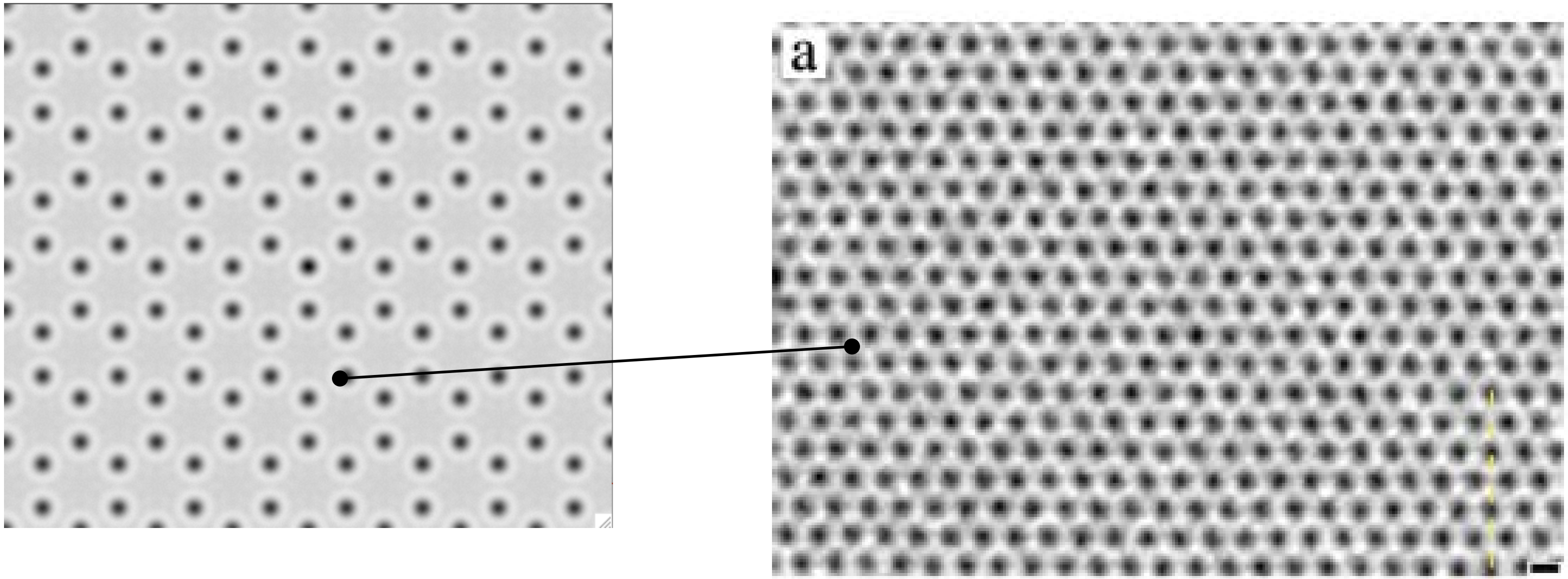
Trilayer Graphene at 80kV, 0 C_S

F. Nelson (INDEX) this conference

Aberration Corrected TEM

First Images of Single Layer Graphene showing atomic structure

TEAM TEM 80 keV Cs = -17 um



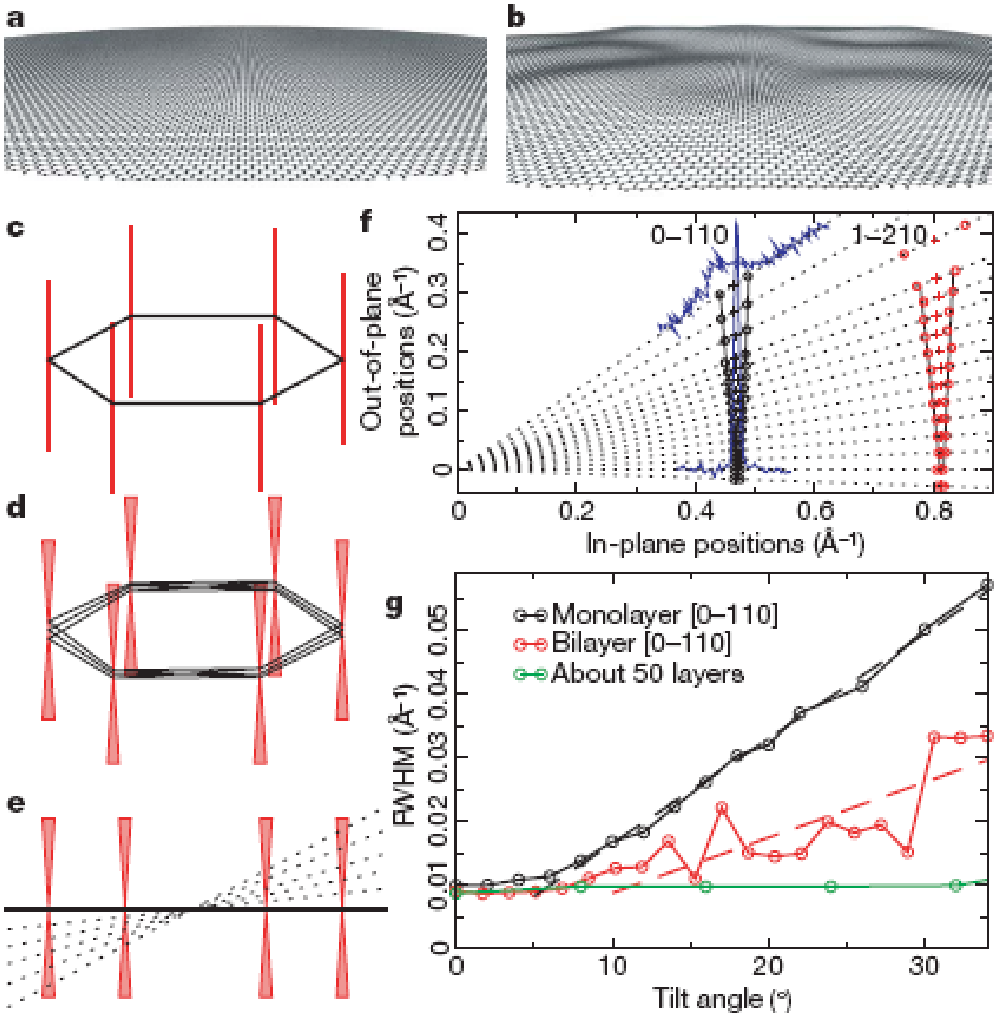
Simulated HR TEM Image at 300 keV with Cs = 0

Figure Courtesy C. Kisielowski - Nano Lett.8, (2008), 3582–3586

Observation of Corrugation: TEM Nano-Diffraction

Length ~ 25 nm

Height ~1 nm

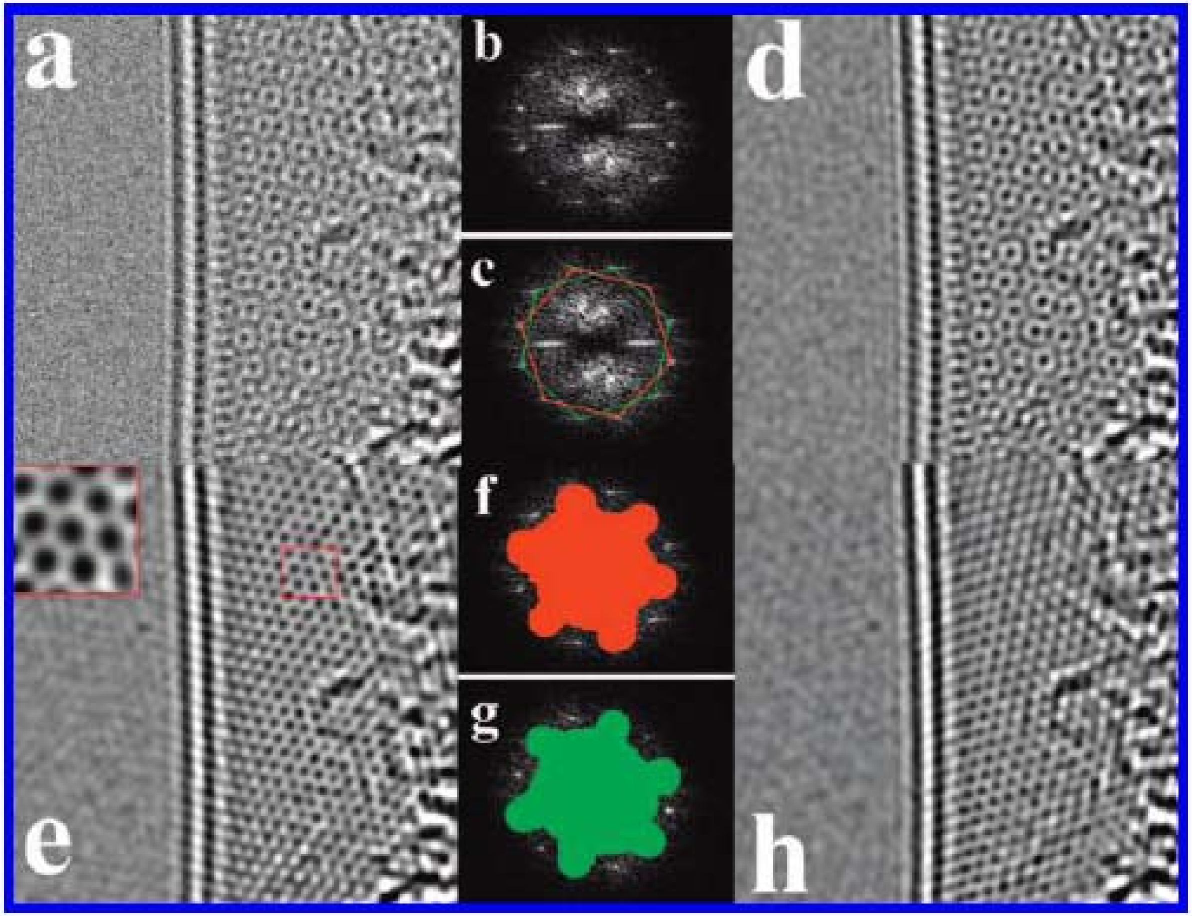


J.C. Meyer, Nature 446, (2007), 60.

2009 – Aberration Corrected TEM of Stacking 2 – Layers with 30º Misorientation

Bi-Layer Graphene

Back Layer



Reconstructed Image

Front Layer

FFT

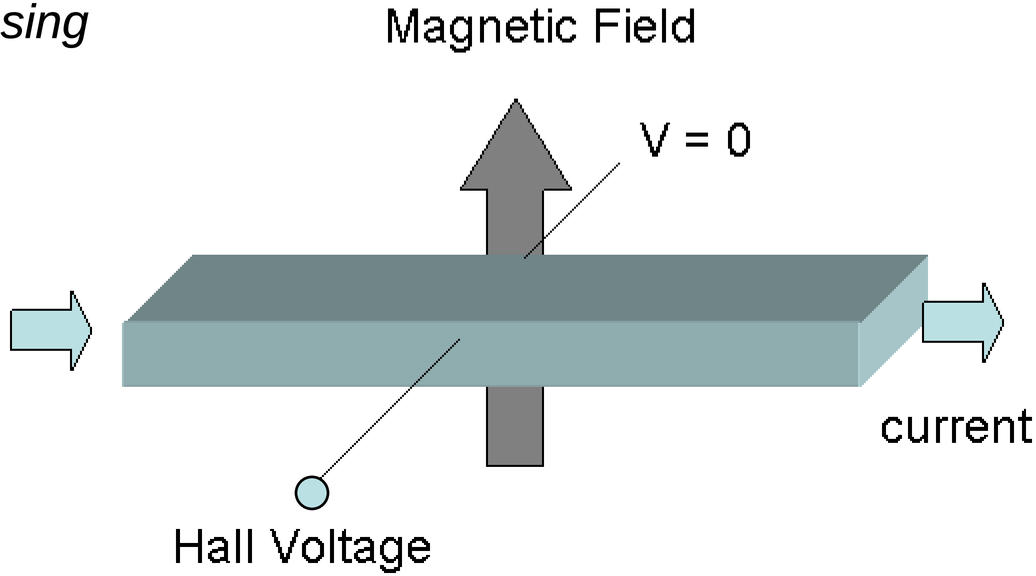
Warner, et. al. (Briggs), Nano Letters (2009), 102

Hall Measurements

Carrier Sheet Density

$N_S = IB / (q|V_H|)$

Determine the sheet resistance R_S using a van der Paw test structure



Mobility

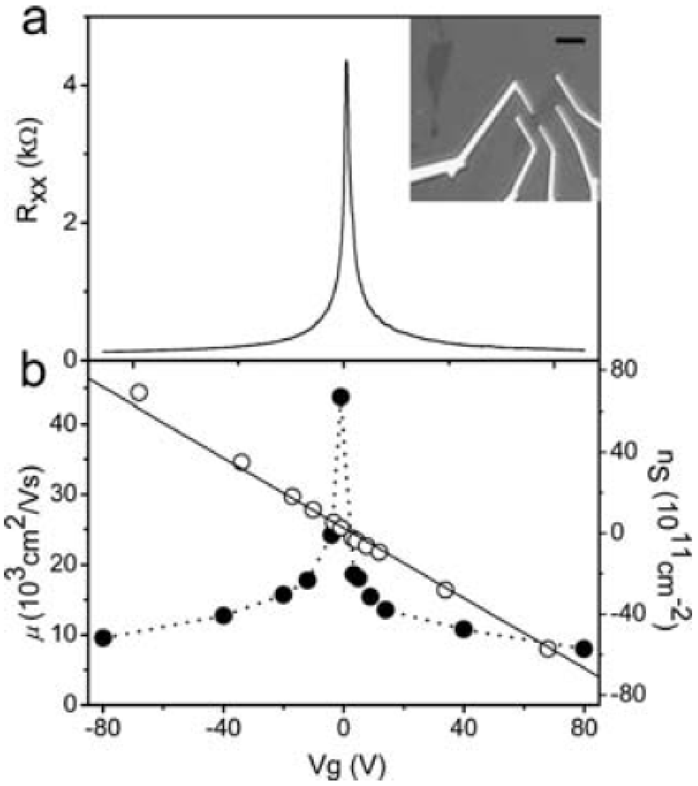
$\mu = |V_H|/(R_S IB) = 1/(qN_S R_S).$

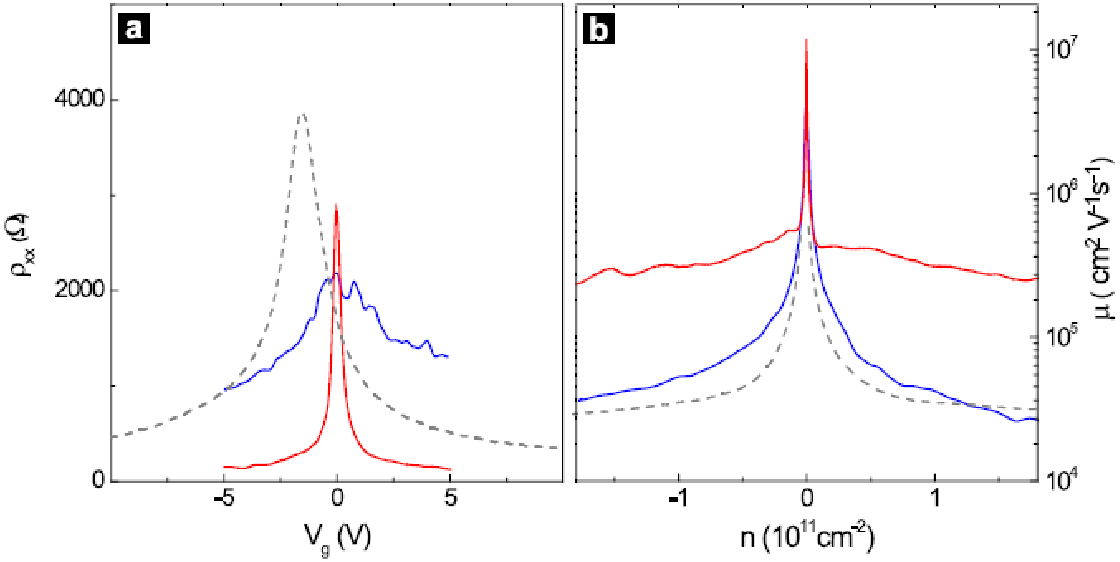
Quantum Hall Effect

$\sigma = \nu e^2/h$ - conductivity

where ν is either and integer or rational fraction

Graphene Mobility Data





Suspended graphene sheet
Red is after annealing

Zhang, et al, Nature 438, 201 (2005)

Bolotin et al Sol. State Com. 146, (2008), 351-355

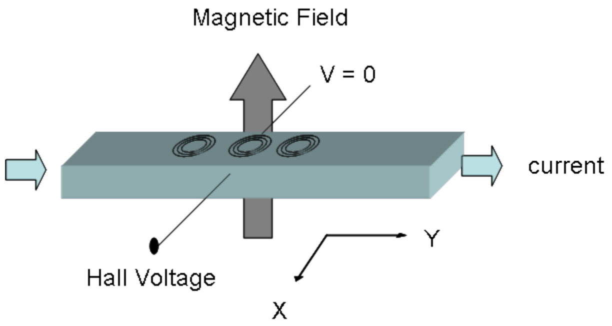
Quantum Hall Effect

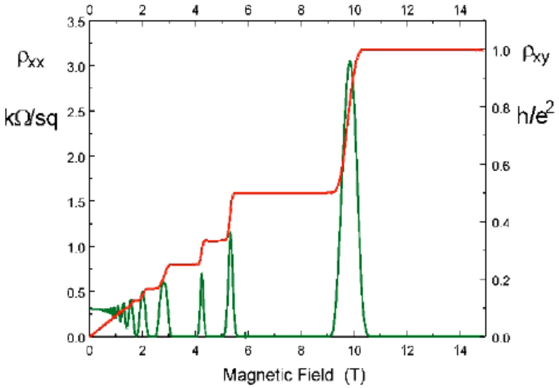
- In a Magnetic Field the Electrons have circular cyclotron orbits
  $\omega_C = (eB/mc)$

- When orbits are treated QM they have discrete energy levels
  - Landau Levels $E_n = (h/2\pi)\omega_C(n+1/2)$

- At certain values of field, energy levels a filled up to N and there is no electron scattering

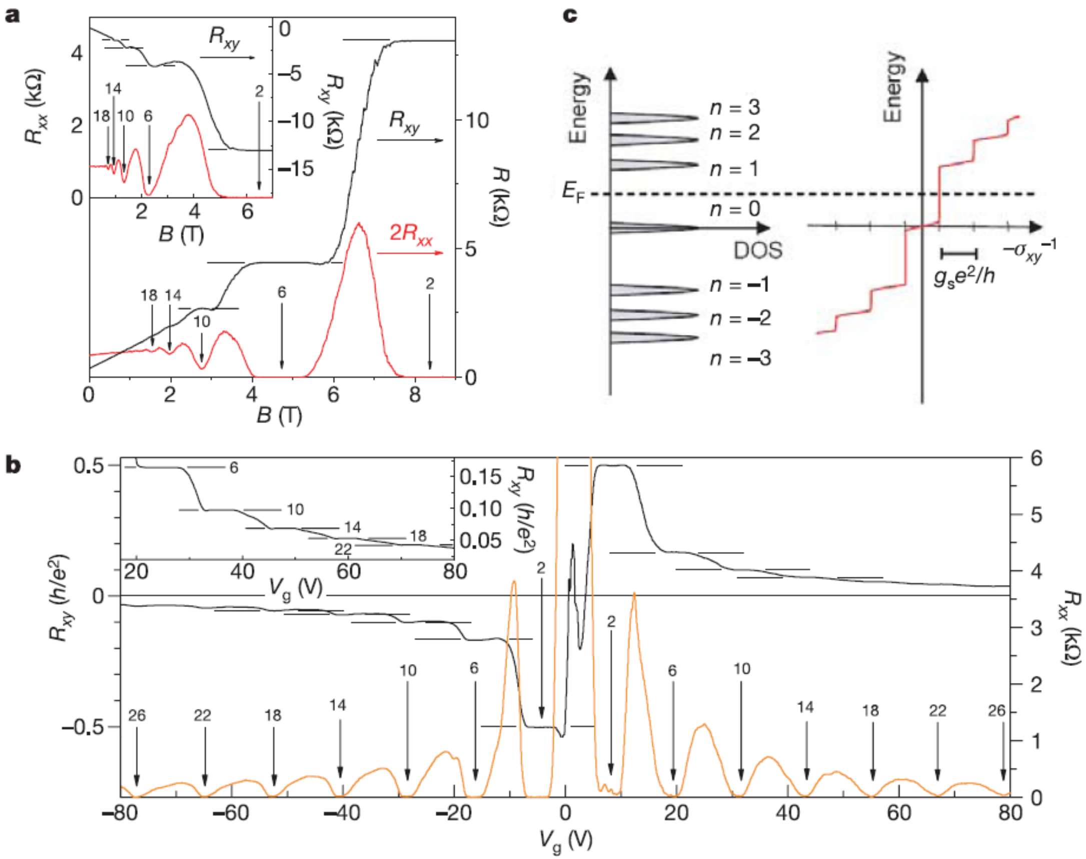
- Conductivity σ will have discrete steps $g_s e^2/h$ where g_s is the degeneracy factor (spin & sublevels) $\sigma \sim N\, e^2/h$





J_x (Hall current) $= \sigma_{xy} E_y$ J_y (current) $= \sigma_{yy} E_y$

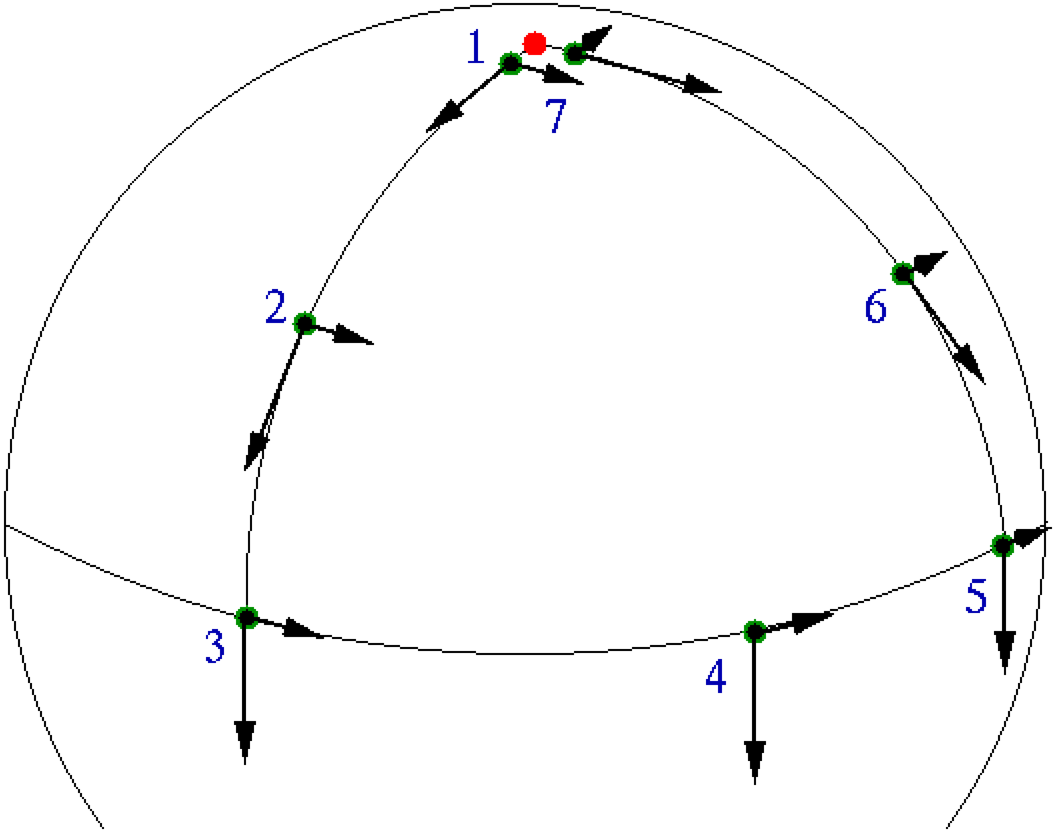
Quantum Hall Effect in Graphene $\sigma \sim (n+1/2)e^2/h$



Stormer and Kim - QHE proves Dirac nature of carriers

Zhang, et al, Nature 438, 201 (2005)

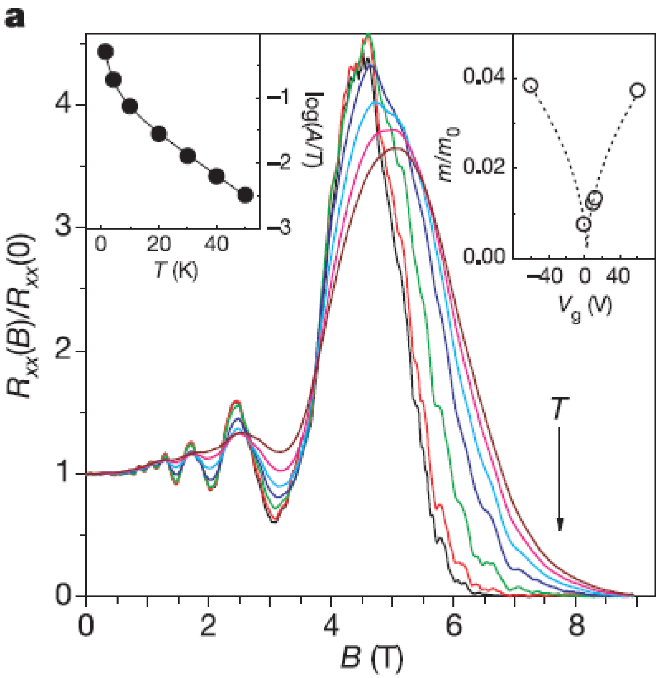
Berry Phase – angle of vector quantities in closed loop path



http://www.mi.infm.it/manini/berryphase.html

Nanoscale Quantum Phenomena

The Berry Phase (angle) in Graphene confirms Dirac particle



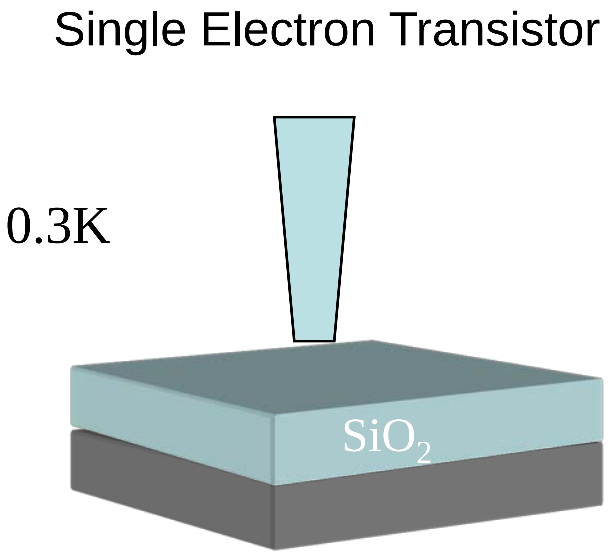
- At low magnetic fields, Shubnikov de Hass oscillations in the resistance Rxx perpendicular to current flow.
- $\Delta R_{xx} = A \cos[2\pi(B_F/B + ½ + \beta)]$
- β (Berry Phase) = ½ for Dirac particles
- B_F is frequency SdH oscillations
- B is magnetic field strength

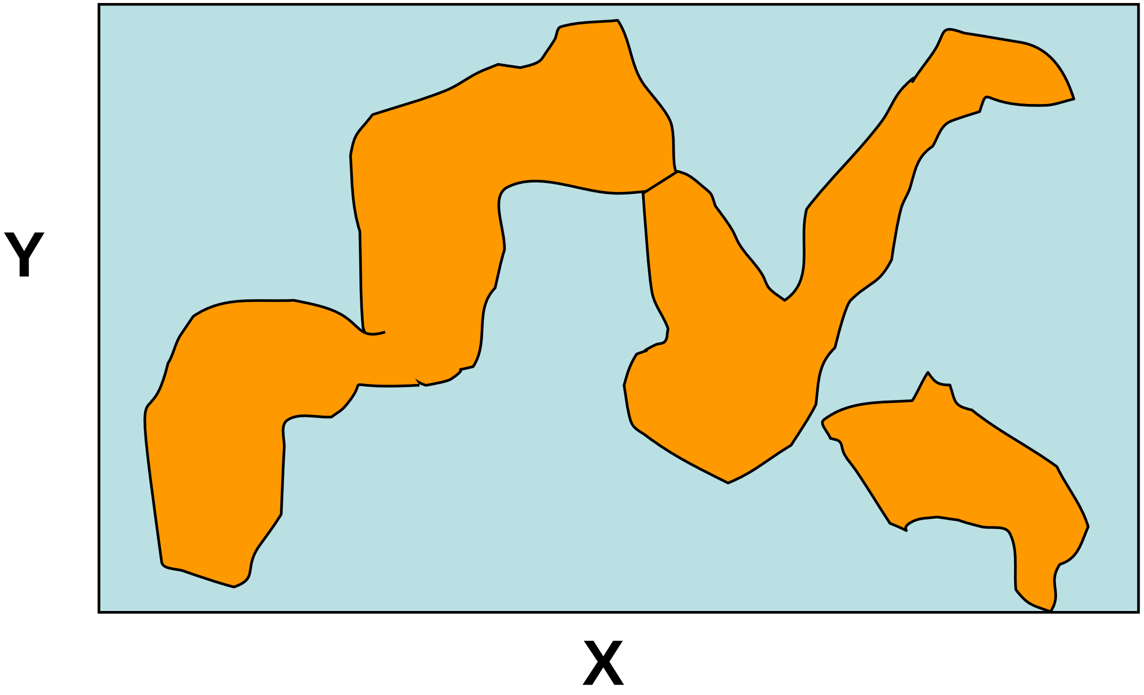
Berry Phase, β, refers to correction to semiclassical dynamics – not needed when a full QM theory is used.

Zhang, et al, Nature 438, 201 (2005)

Single Electron Microscopy Electron Hole Puddles – Are they due to Graphene Corrugation from SiO_2?

The intrinsic disorder length scale in graphene is ~ 30 nm.

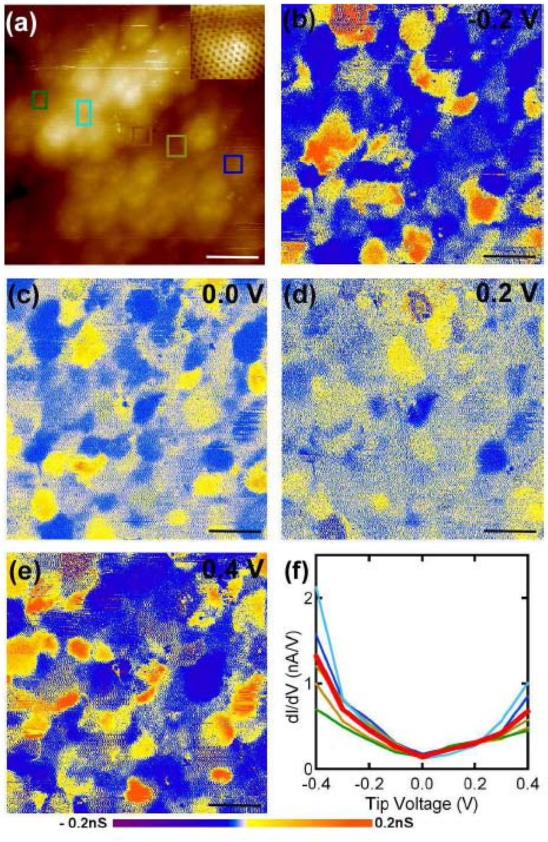




“The SET tip is capable of measuring the local electrostatic potential with microvolt sensitivity and a high spatial resolution close to its size.”

J. Martin, et al, Nature Physics, 4, (2008), 144-148.

Observation of Graphene Corrugation by STM



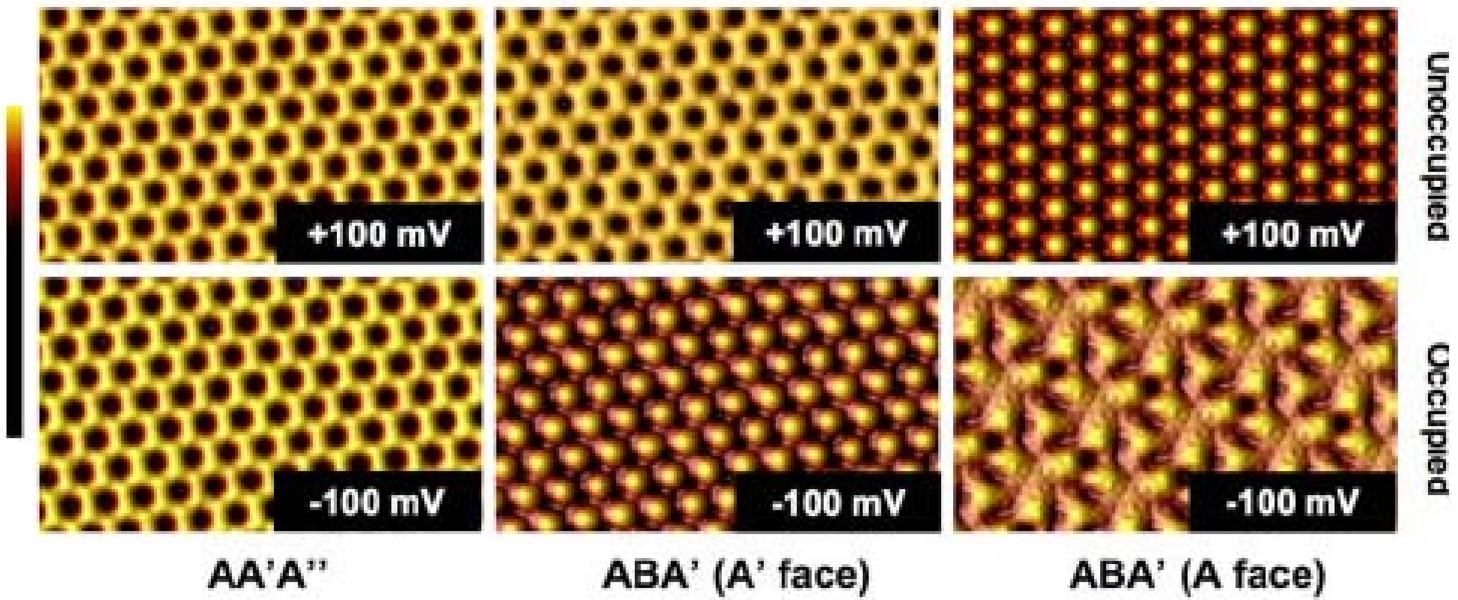
Corrugation has a height variation of 5 A over an area of 30 30 nm^2.

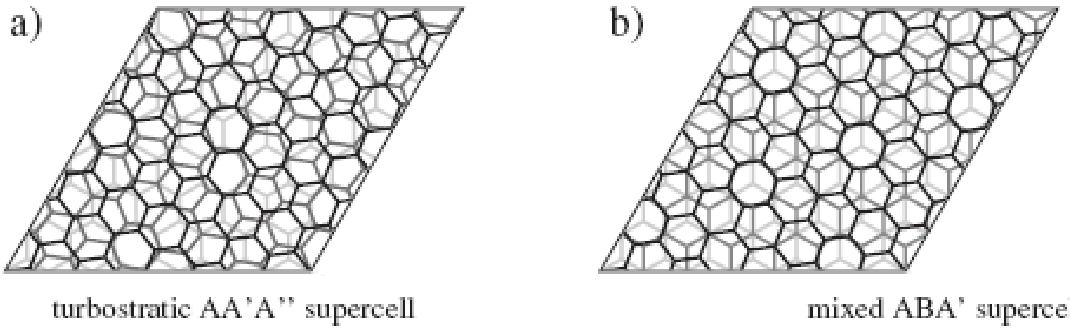
Lateral extent of these corrugations ~ few nanometers

Corrugation mimics the SiO_2 surface

Deshpande, Bao, Miao, Lau, and LeRoy, Spatially resolved spectroscopy of monolayer graphene on SiO2

STM Observation of Stacking Misorietation



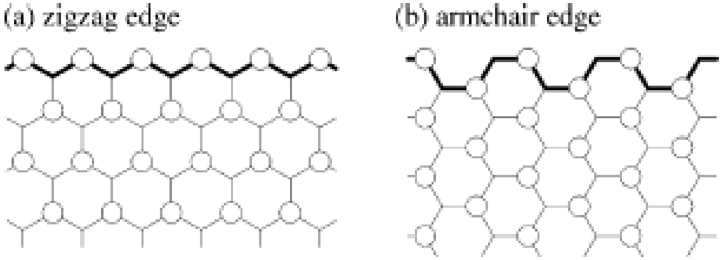


Latil, Meunier, and Henrard, PRB 76, 201402_R (2007)

3 layer graphene on SiC

Graphene Ribbons

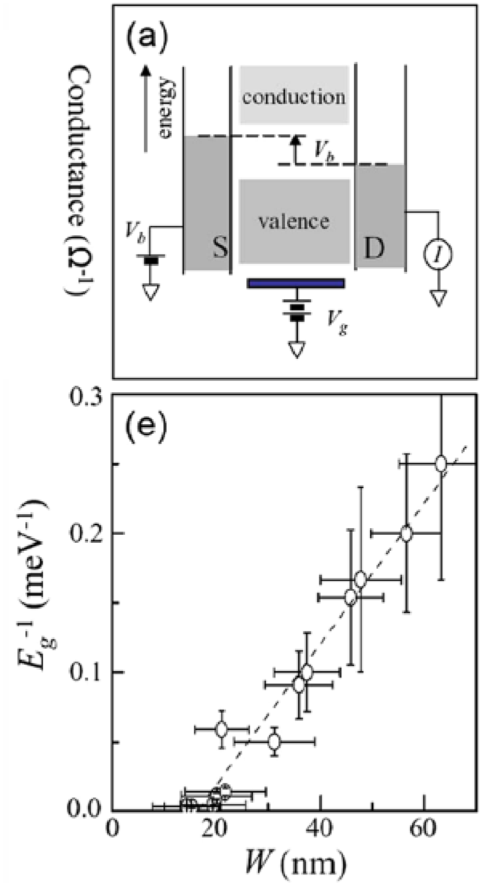
Can We Measure properties of Ribbons?



(a) zigzag edge (b) armchair edge

Fig. 6. GNR edges. (a) Zigzag edge, (b) armchair edge

Band Gap



Width of Graphene NanoRibbon

Han, et al (Kim’s Group), PRL 98, 206805 (2007)

What we can Measure

- Where graphene is (for some samples)
- Number of graphene layers & orientation
- Corrugation
- Electrical – mobility, carrier density, conductance

Conclusions

- Graphene displays novel properties due to nanoscale dimensions and unique electronic structure

- Metrology must continue to advance to meet needs of new materials such as graphene

- Despite these advances- metrology and device fabrication are amazingly difficult

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